

BENCH SCALE CO-PYROLYSIS OF A LOW RANK COAL AND A PETROLEUM RESIDUE

I. Suelves, R. Moliner and M.J. Lázaro

Instituto de Carboquímica (CSIC). María de Luna, 12. 50015 Zaragoza (Spain)

INTRODUCTION

During coal pyrolysis, both degradation processes that create free radicals and crosslinking reactions, happen simultaneously. To increase the liquid yields obtained from coal pyrolysis radical stabilisation should be promoted and crosslinking reactions should be decreased^{1,3}. However, coal hydrogen content is not high enough to promote this radical stabilisation and so that, hydrogen should be provided from other sources. One of the most promising ways of increasing the hydrogen content is provide it from hydrocarbon materials, specially hydrocarbon wastes that can be co-pyrolyzed with coal^{4,7}. This way two benefits are expected: first coal may enhance the conversion of the hydrocarbon material and beside this the presence of the waste would improve the quality of the products obtained from coal. Petroleum residue is a very interesting material that observes the main characteristics needed to be used in this type of processes: hydrogen content, aliphatic nature, etc. However, there are few references in literature on this subject because the most important works on co-utilization of coal and petroleum residues are related with catalytic coprocessing reactions, using high hydrogen pressures. In our previous works at analytical scale we have shown that there is a synergetic effect for the production of some interesting compounds like light olefins and BTX when coal and petroleum residue are co-pyrolyzed^{8,9}. Therefore at this scale, secondary reactions were disfavoured and there was no possibility of stabilising mass balances or evaluating the influence of co-pyrolysis on char formation. For that reasons, the main objectives of this work are: (i) to evaluate the interactions between coal and petroleum residue during co-pyrolysis at bench scale and (ii) to study the influence of the experimental conditions on char formation.

EXPERIMENTAL

Different experimental series were carried out, each of them dedicated to the study of the influence of temperature, pressure and petroleum residue mass ratio on the mixture behaviour. Temperatures used were 600, 650 and 700°C; pressures, 0.1, 0.5 and 1 MPa and mass ratio (Coal/PR) 70/30 and 50/50.

Materials

Samca coal (Teruel, Spain) and a petroleum vacuum residue (PR) have been used in this work. Samca is a subbituminous coal with high volatile content and with high sulphur and oxygen content. The petroleum residue proceeds from the distillation of different crudes and has been submitted by REPSOL (Puertollano, Spain). The main characteristics of these materials have been described in our previous works^{8,9}.

Experimental installation

Bench scale pyrolysis unit used in this work has been shown elsewhere¹⁰. In summary it consists of an oven heated reactor with two different parts; the bottom of the reactor, where pyrolysis happens, is filled with a ceramic rings bed. The sample is feeded from the upper part and falls into the reactor by gravity. When the sample is introduced, the reactor has reached the pressure and temperature conditions of the pyrolysis run. Pyrolysis products are recovered from the bottom of the reactor swepted by a nitrogen stream. They are cooled in a Peltier effect cooler. Liquids are collected in a liquid-cyclone and gases are collected in a gas sampling bag which volume is measured after each run.

Sample preparation

First coal and PR were pyrolyzed alone and then as a mixture. Preparation of the mixtures was as follows: PR was first solved in THF and then coal was added. The mixtures were subsequently sonicated. After 15 minutes, THF was evaporated by heating under vacuum. The dried samples were grounded to <0.2 mm. A cryogenic grinding technique was used in order to increase the grindability of the sample and to improve the homogeneity of the mixtures. Samples of around 10g were used in each run

Analytical Methods

The ponderal yields of char and liquids were determined by direct weight whereas gas global yields were calculated from the sum of the individual yields of each of the components obtained by gas-chromatography. A run was considered as a valid one if the ponderal yield sum of all recovered products was higher than 95%. Global results were normalised to 100% in order to facilitate comparison between runs.

Gases were analysed by gas chromatography using three separate analytical methods: a packed column of Molecularsieve 13X with nitrogen as carrier gas and TCD detection for hydrogen; two packed columns: Molecularsieve 13X and Porapak with helium as carrier and TCD

detection for permanent gases; an alumina capillar column with helium as carrier and FID detection for C_1 - C_6 hydrocarbons. Hydrocarbons chromatographed between n-pentane and n-hexane were accounted for together as C_5 . In the same way, compounds chromatographed between n-hexane and benzene were accounted for as C_6 . Quantification of gas components was carried out by means of standard gas mixtures.

Liquids were formed by the organic phase, tar and water. The separation of tar and water was very difficult, so that they were weighed all together. Liquids were analysed by GC/MS. All compounds present in liquids were identified by using a computerised library of mass spectra. Tri and tetramethylbenzenes were accounted for as "alkyl-benzene" and all the compounds chromatographed between naphthalene and phenanthrene were accounted for as "2-3 rings". Quantitative composition of liquids was determined by the internal standard method using octane as the internal standard.

RESULTS AND DISCUSSION

If there is no interaction between the components of the mixture, the yields obtained in the co-pyrolysis (experimental values) should be equal to the sum of yields obtained in the pyrolysis of the individual components (theoretical values). In this way, by comparing experimental and theoretical values, the existence of a synergetic effect in the yields of the most interesting pyrolysis products and the influence of the experimental conditions have been evaluated. First the evolution of the char, liquid and gases yields as a whole was studied and after that, the yields of the most interesting gaseous products and the evolution of the liquid fraction was evaluated.

Evolution of synergism with temperature

The 70/30 mixture was copyrolyzed at 600, 650 and 700°C. At 600°C the experimental char yield is higher than the theoretical one and there is an experimental decrease on liquid and gases production compared with the theoretical one. Analysing the evolution of the individual products only a higher experimental yield is observed for CO_2 , SH_2 and methane. This fact can be related with the enhancing of cross-linking reactions that favour the evolution of this kind of gases as a by-product of char formation^{11,12}. At 700°C although there is a better liquid production than working at 600°C and even the experimental yields of some interesting gaseous products are higher than the theoretical ones, the experimental char production is also very high.

Figure 1 show the comparison between the experimental and theoretical yields obtained working at 650°C. It can be observed from this figure that the theoretical and experimental char yields are almost equal and that the experimental liquids yield increase in detriment of the gases one after the co-pyrolysis of the mixture. The comparison between the experimental and theoretical yields of the individual components of the gas fraction shows that there is a decrease in the experimental yield of carbon oxides and SH_2 and that on the other hand, the experimental yields for light olefins: ethylene, propylene and C_4 olefins are higher than the theoretical ones and so that, a favourable synergetic effect is observed. At 650°C there is also an important synergetic effect for the production of all aromatic compounds, specially for benzene derivatives.

During pyrolysis of hydrocarbon nature materials^{1,13} two types of reactions are suggested: first degradative processes that produce small radicals and then recombative reactions were this small radicals take part. When secondary reactions happen via Diels-Alder, aromatic compounds are obtained. This seems to be a good explanation for 70/30 mixture behaviour: first PR is degraded and due to its high aliphatic fraction¹ it leads to a great ethylene and other light olefins production. Then the ethylene radical reacts in gas phase with the small radicals obtained from coal and so that, BTX experimental production increases. In summary it can be concluded that the main objectives of this work are achieved, working with mixtures in a mass ratio of 70/30 at 0.1MPa and 650°C.

Evolution of synergism with pressure

All runs studying the evolution of yields with pressure were carried out at 650°C. The good results obtained working at atmospheric pressure and 650°C do not occur when pressure increases. There are no important differences between working at 0.5 or 1MPa. Figure 2 shows the comparison between the theoretical and the experimental yields obtained at 1MPa. The experimental char yield is higher than the theoretical one, in detriment of gases and liquids yields. The evolution of the individual components of the gas phase shows that there is no synergetic effect for any of the interesting compounds. Moreover this, working at high pressure the liquid fraction could not be evaluated. The liquids obtained have very high water content and solid suspensions and for that reason they could not be chromatographed. So, increasing pressure seems to disfavour gas phase reactions, probably because intraparticle reactions that lead to an increase on char yield¹⁴ are enhanced.

Evolution of synergism with petroleum ratio in the mixture

Figure 3 shows the comparison between the theoretical and the experimental yields obtained for the 50/50 mixture working at 0.1MPa and 650°C. It can be observed an important increase in the experimental char yield comparing with the theoretical values which contrast with the similar experimental and theoretical values obtained for the 70/30 mixture. There is also a slight

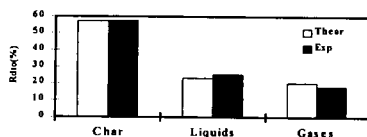
experimental increase for the production of CO_2 , SH_2 , methane and ethylene but the most important fact that should be taken into account is the bad results obtained for the liquid fraction. The only synergetic effect happens for the higher weight aromatic compounds. For benzene, toluene, xylene and alkyl-benzenes, the theoretical yields are higher than the experimental ones. From these results it can be concluded that the increase in the petroleum residue ratio in the mixture disfavours tar forming reactions while enhances char formation. One of the suggested explanations for the behaviour of the 50/50 mixture is that although PR degradation occurs, when PR mass ratio in the mixture increases, the formed radicals can not react with the radicals emerging from coal and this way secondary reactions in gas phase that lead to the BTX formation are not allowed, and only intraparticle reactions that increase char formation are enhanced. A more detailed study of these processes and probably the analysis of the nature of chars obtained would provide enough information to consolidate the present explanation.

REFERENCES

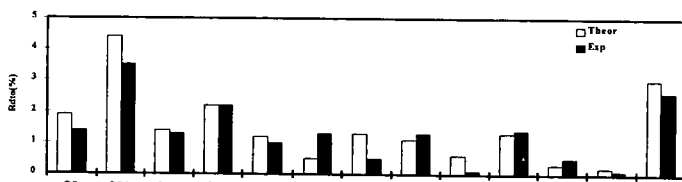
1. Ofosu-Asante K., Stock L.M., Zabransky R.F. (1989). Fuel. Vol.68, 567-572.
2. Hayashi J., Kawakami T., Taniguchi T., Kusakabe K., Morooka S. (1993). Energy&Fuels, 7, 1118-1122.
3. Miura K., Mae K., Asaoka S., Hashimoto K. (1991). Energy&Fuels, 5, 340-346.
4. Fontana A., Braekman-Danheux C., Laurent P. (1995). "Coal Science and Technology 24". (Elsevier. J.A. Pajares, J.M.D. Tascón Eds.) pp 1089-1092.
5. Laurent P., Braekman-Danheux C., Fontana A., Lecharlier M. (1997). ICCS 97. Vol II. (Ziegler et al Eds.), 837-840.
6. Palmer S.R., Hippo E.J., Tandon D., Blankenship M. (1995). "Coal Science and Technology 24". (Elsevier. J.A. Pajares, J.M.D. Tascón Eds.) 29-33.
7. Klose W., Stuke V. (1993). Fuel Processing Technology, 36, 283-289.
8. Moliner R., Suelves I., Lázaro M.J. (1998). Energy&Fuels. Vol.12, N°5, 963-968.
9. Suelves I., Lázaro M.J., Moliner R. (1997) ICCS 97. Vol. II 745-748 (Ziegler et al Eds.)
10. Moliner R., Lázaro M., Suelves I. (1997). Energy&Fuels. Vol.11, N°6, 1165-1170.
11. Ibarra J.V., Cervero I., García M., Moliner R. (1990). Fuel Processing Technology, 24, 19-25.
12. Suuberg E.M., Lee D., Larsen J.W. (1985). Fuel. Vol.64, 1668-1671.
13. Moliner R. (1995). Final Report Project CECA 7220-EC/763.
14. Moliner R., Ibarra J.V., Lázaro M.J. (1994). Fuel. Vol.73, n°7, 1214-1220.

Figure 1. Experimental and theoretical yields: Samca/RP (70/30). P=0.1MPa. T=650°C.

A) Mass balance



B) Gases



C) Liquids

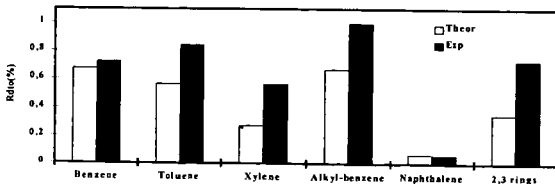
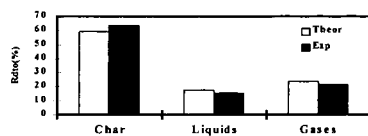


Figure 2. Experimental and theoretical yields: Samca/RP (70/30). P=1MPa. T=650°C.
A) Mass balance



B) Gases

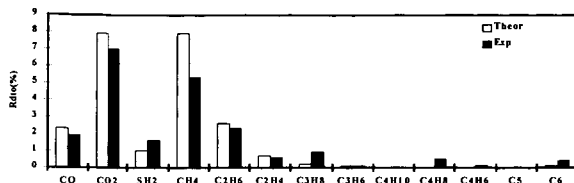
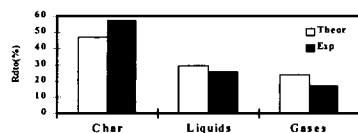
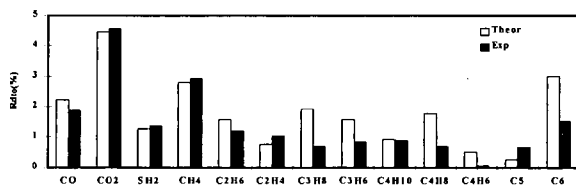


Figure 3. Experimental and theoretical yields: Samca/RP (50/50). P=0.1MPa. T=650°C.
A) Mass balance



B) Gases



C) Liquids

